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Guest displacement in silicon clathrates

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We study both theoretically and experimentally the structure of the doped silicon clathrate $\text{II Na}_x\text{Si}_{34}$. We find that contrary to published works, the sodium atoms do not retain the T_d symmetry inside the Si_{28} cages and move about 1 Å away from the center of the cage. This displacement, in conjunction with that of a sodium atom in an adjacent Si_{28} cage, leads to a “dimerization” of sodium atoms. As a consequence, Rietveld refinements of x-ray diffraction spectra and transport, vibrational, and electronic properties must be revisited.

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I. INTRODUCTION

Clathrates^{1–3} are cagelike compounds allowing endohedral doping by intercalation of guest atoms inside the cages of the host network. In particular, silicon clathrates have received increasing attention over the past decade, following the observation of unusual and interesting properties related to the guest-host interaction. These properties include superconductivity,⁴ wide-optical band gap devices,⁵ hardness,⁶ high-doping semiconductors, and thermoelectric applications.⁷ The frameworks built from silicon adopt a cagelike geometry around the guest atoms. Among the numerous clathrate structures, the most studied are $X_8\text{Si}_{46}$ (type I) and $X_n\text{Si}_{34}$ with $0 < n < 6$ (type II) compounds. Both lattices correspond to the triplicate periodic arrangement of fullerene-like molecules Si_{20} and Si_{24} (clathrate I) or Si_{20} and Si_{28} (clathrate II), sharing their common faces. Clathrates have been investigated by numerous spectroscopies including nuclear magnetic resonance (NMR),^{8–13} electron spin resonance (ESR),^{14,15} x-ray photoelectron spectroscopy (XPS),^{13,16} extended x-ray absorption fine structure (EXAFS),¹⁶ and vibrational spectroscopies.^{17–19} In this article, we investigate both theoretically and experimentally, through EXAFS spectroscopy, the structure of the clathrate II lattice with sodium as guest. The *ab initio* calculations are performed within the framework of the local density approximation (LDA)²⁰ and the generalized gradient approximation (GGA)²¹ of the density functional theory (DFT).²² Contrary to other published work, we find that the $Fd\bar{3}m$ space group is inconsistent with our results. An instability (soft phonon modes) in Si_{28} cages breaks the symmetry of the lattice involving an off-center displacement of the encapsulated sodium atom. The Rietveld refinements, the ²³Na NMR chemical shift analysis and the electronic properties, have to be reconsidered in the light of this effect.

II. EXPERIMENTAL PROCEDURE AND RESULTS

Silicon clathrate samples are synthesized in two steps:¹ the synthesis of the precursor (silicide NaSi) and its pyroly-

sis. The silicide NaSi is prepared by treating stoichiometric mixtures of Si and Na elements. The silicide is then transferred in a vacuum chamber and heated at moderate temperature (700–1000 K). During the heating, the samples lose alkali. The stoichiometry can be adjusted by incorporating metallic alkaline vapor and is determined by x-ray diffraction and/or by the flame emission technique. We have analyzed two samples with the stoichiometry $x=2$ and $x=6$. In the former, sodium fills all Si_{28} cages, Si_{20} cages remaining empty, while the stoichiometry $x=6$ corresponds to the filling of all the cages. Note that the low stoichiometry sample is obtained by filling a quasiempty Si_{34} clathrate, not by emptying a filled one. Table I gives the expected symmetry for silicon and sodium atoms.

Na *K*-edge absorption spectra have been recorded at three temperatures 20, 100, and 300 K in the fluorescence mode. The measurements have been done on beam line SA32 located at the 800 MeV positron storage ring super-ACO in Orsay, France. More details are given in an earlier paper.¹⁶ EXAFS oscillations $\chi(k)$ have been extracted following the standard procedure. The EXAFS signals have been calculated within the framework of *ab initio* self-consistent real space multiple-scattering FEFF8 code.²⁴ We emphasize that no adjustable parameters other than the absorption edge and the position of Na atoms are used. These parameters are manually adjusted. This ensures a relevant EXAFS analysis. Figure 1 displays the experimental EXAFS Fourier transform $g(R)$ of $k\chi(k)$ (pseudoradial pair distribution function) for $\text{Na}_2\text{Si}_{34}$ and $\text{Na}_6\text{Si}_{34}$ along with simulation results with Na at the center of the Si_{28} cage or moved away from the center. The first observation we can make is that there is a single first-neighbor peak for $\text{Na}_2\text{Si}_{34}$ and the agreement with the simulations using just Si_{28} cages is a clear evidence for preferential filling of large cages, when starting from an empty clathrate.

The EXAFS simulations are done using self-consistent scattering potentials (absorbing Na, Na@ Si_{20} , Na@ Si_{28} , and Si), calculated with the sodium atoms at the center of the

TABLE I. Crystallographic data for type-II silicon clathrates $\text{Na}_6\text{Si}_{34}$. For dimerized clathrate, d is the sodium displacement from the center of a Si_{28} cage, along the (111) direction.

Name		Clathrate II $\text{Na}_6\text{Si}_{34}$						
Space group		$Fd\bar{3}m$, origin at center $\bar{3}m$						
Lattice constant ^a		$a = 14.6429 \text{ \AA}$						
		x	y	z				
x, y, z positions ^a , point	Si	1/8	1/8	1/8	$4\bar{3}m$	8	a	
symmetry, number of	Si	0.7827	0.7827	0.7827	$3m$	32	e	
positions, Wyckoff	Si	0.8169	0.8169	0.6288	m	96	g	
notation	Na	0	0	0	$\bar{3}m$	16	c	
	Na	3/8	3/8	3/8	$\bar{4}3m$	8	b	
Name		Clathrate II $\text{Na}_6\text{Si}_{34}$ dimerized						
Space group		$Fd\bar{3}m$, origin at center $\bar{3}m$, plus F cubic lattice for $\text{Na}@_{\text{Si}_{28}}$						
Lattice constant ^a		$a = 14.6429 \text{ \AA}$						
		x	y	z				
x, y, z positions ^a , point	Si	1/8	1/8	1/8	$4\bar{3}m$	8	a	
symmetry, number of	Si	0.7827	0.7827	0.7827	$3m$	32	e	
positions, Wyckoff	Si	0.8169	0.8169	0.6288	m	96	g	
notation	Na	0	0	0	$\bar{3}m$	16	c	
		Na@ Si_{28} F cubic lattice						
	Na	$3/8 + d/(a\sqrt{3})$	$3/8 + d/(a\sqrt{3})$	$3/8 + d/(a\sqrt{3})$	$3m$	4		
	Na	$5/8 - d/(a\sqrt{3})$	$5/8 - d/(a\sqrt{3})$	$5/8 - d/(a\sqrt{3})$	$3m$	4		

^aRef. 23

cages. Although the EXAFS spectrum is, of course, dependent on the sodium atom position, we have found that the way the self-consistent potentials are calculated (sodium atom at the center or off-center) has almost no incidence on the result. We have also noticed that the results were unchanged whether two neighboring $\text{Na}@_{\text{Si}_{28}}$ atoms were displaced each one towards the other or not. This emphasizes that EXAFS is only sensitive to the very local environment of the absorbing atom.

The best fit for $\text{Na}_2\text{Si}_{34}$ is obtained when the sodium atom

moves away by 1 \AA from the center of the Si_{28} cage towards the center of a hexagonal face (that is to say, overall in the direction of a neighboring sodium atom in an adjacent Si_{28} cage). For $\text{Na}_6\text{Si}_{34}$, the best fit is obtained with the $\text{Na}@_{\text{Si}_{28}}$ displaced in the same way and the $\text{Na}@_{\text{Si}_{20}}$ at the center of the cages, the value of the displacement being 2 \AA . This value is overestimated and is due to the fact that in this case the signal is dominated by the contribution of Na atoms in Si_{20} cages which are twice as many as $\text{Na}@_{\text{Si}_{28}}$. The contribution to the signal of Na atoms in Si_{20} cages is the highest

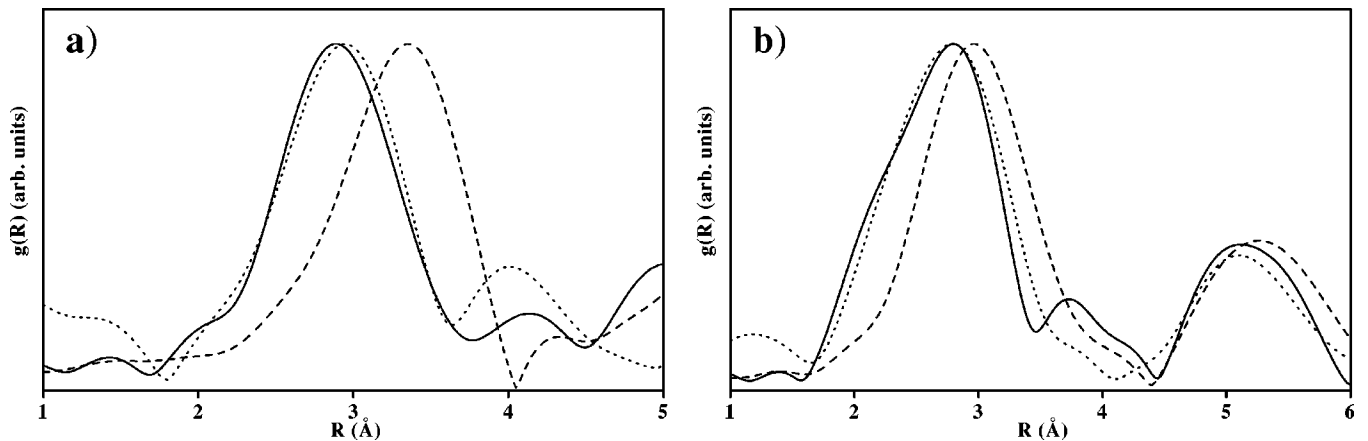


FIG. 1. Fourier transform $g(R)$ of the EXAFS signal $k\chi(k)$ of $\text{Na}_2\text{Si}_{34}$ (a) and $\text{Na}_6\text{Si}_{34}$ (b) at $T=20 \text{ K}$. Dotted lines: experimental spectrum. Dashed lines: fit of the data obtained with the Na atoms placed at the center of the cages. Solid lines: fit of the data obtained with the Na atoms displaced in the Si_{28} cages. For $\text{Na}_6\text{Si}_{34}$, the Na atoms in Si_{20} cages are kept at the center of the cages.

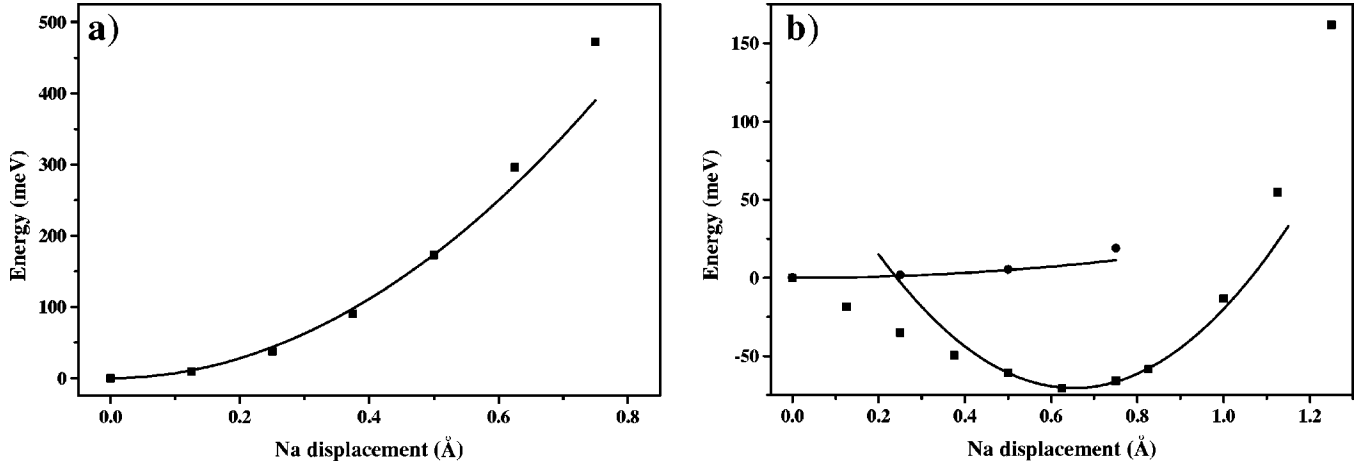


FIG. 2. (a) Potential energy curve (squares) for a sodium atom in a $\text{Si}_{20}\text{H}_{20}$ cage. (b) Potential energy curves for a sodium atom in a $\text{Si}_{28}\text{H}_{28}$ cage (circles) and for two sodium atoms in two adjacent Si_{28} cages ($\text{Si}_{50}\text{H}_{44}$), moving symmetrically towards each other (squares). The solid lines are parabolic fits to the curves.

peak at 2.9 Å. The agreement between experiment and simulation regarding this peak shows that the Na atoms in Si_{20} cages remain at the center of the cages. The displaced Na atoms in Si_{28} cages are only responsible for the shoulder at 2.3 Å. The resulting value of the displacement of sodium in Si_{28} is therefore less accurate (~ 0.5 Å of uncertainty) and we give more credit to the value deduced from $\text{Na}_2\text{Si}_{34}$ (~ 0.2 Å of uncertainty). Nevertheless, as can be seen in Fig. 1, the existence of the displacement is undoubted in both cases since the simulated signal with Na atoms at the center of the cages is unable to fit the experimental signal.

III. COMPUTATIONAL ANALYSIS

To further study the sodium displacement, we have performed *ab initio* DFT calculations of ground-state energy and phonon density of states for both $\text{Na}_2\text{Si}_{34}$ and $\text{Na}_6\text{Si}_{34}$. We have used the PWSCF package²⁵ which is a code based on a pseudopotential^{26,27} and a plane wave approach. For structure optimization, the Brillouin zone has been sampled by a $4 \times 4 \times 4$ Monkhorst and Pack grid,²⁸ and a 16 Ry cutoff energy has been used. To evaluate the energy of the ground state, we have adopted a finest $8 \times 8 \times 8$ k grid and a 20 Ry cutoff energy. The phonons have been evaluated within the framework of the linear response implemented in the PWSCF code. We have used a $4 \times 4 \times 4$ k grid and a 16 Ry cutoff energy to calculate the phonons, only at $k = \Gamma$, in $\text{Na}_2\text{Si}_{34}$ and $\text{Na}_6\text{Si}_{34}$ clathrates.

In the case of $\text{Na}_2\text{Si}_{34}$, we have observed a vibrational mode of T_d symmetry associated with the sodium in the Si_{28} cages with an “imaginary” frequency (i.e., a negative force constant). This phonon instability reveals that the position at the center of the Si_{28} cages is unstable for sodium. Accordingly, for the ground-state energy calculation, a displacement of sodium by 0.25 Å from the center towards a hexagonal face is found to be slightly stable (1 meV). In the case of $\text{Na}_6\text{Si}_{34}$, the frequency of the T_d symmetry mode is very low, about 25 cm^{-1} , meaning that the Na atom is surrounded by a flat potential. The Na atom is free to move in the Si_{28}

cages on relatively long distances without any significant effect on the ground-state energy (within the precision of the calculation). However, we have noticed that the k -space sampling grid is of prime importance for the observation of the displacement as well as for its numerical value (particularly if it contains the k points at the Fermi level most affected by the displacement).

To overcome this problem, we have restricted the calculations to a “piece of clathrate” consisting of one or two filled Si_{28} cages or one filled Si_{20} cage. The positions of the Si atoms were strictly those of the clathrate network and the dangling bonds were passivated with hydrogen atoms.³⁰ These calculations have been performed using the SIESTA code³¹ based on atomiclike numerical orbitals, in the LDA. We have used a fcc unit cell with a 200 Bohr lattice parameter and a real space grid equivalent to a plane wave cutoff energy of 80 Ry. We have used a double-zeta basis for H, and a polarized double-zeta basis for Si and Na. Using one single cage simulates a Na atom without any sodium neighbor in the adjacent cages of the clathrate, while with two adjacent Si_{28} cages filled with Na, we can study the influence of a neighboring sodium atom, as it is the case in clathrate for high enough Na stoichiometry. We have computed the potential energy curve by freezing every silicon and hydrogen atoms (the latter were previously relaxed), moving only the sodium in the cages. Doing so, we have followed the protocol previously used by Dong *et al.*²⁹ The direction of displacement was towards the center of a pentagonal face in the Si_{20} cage and towards the center of a hexagonal face in the Si_{28} cage. In the case of two adjacent Si_{28} cages, the two Na atoms were moved symmetrically closer to each other.

Figure 2 displays the corresponding potential energy curves. First of all, the potential energy curve of $\text{Na}@ \text{Si}_{20}\text{H}_{20}$ [Fig. 2(a)] has its minimum at the center of the cage meaning that the sodium atom stands at the center of the smallest cage. For one $\text{Na}@ \text{Si}_{28}\text{H}_{28}$ [Fig. 2(b)] the potential energy still presents a minimum at the center of the cage but the potential well is much less pronounced than in $\text{Si}_{20}\text{H}_{20}$, meaning that the coupling of the sodium atom with

the silicon cage is weaker. In the case of two adjacent Si_{28} cages [Fig. 2(b)], the minimum of the potential energy is found at a displacement of around 0.65 Å on the axis joining the centers of the two Si_{28} cages; a value in fairly good agreement with EXAFS spectroscopy of $\text{Na}_2\text{Si}_{34}$. The atoms of the Na “dimer” are now separated by about 5 Å instead of 6.3 Å when they are at the center of the cages. The energy difference between this minimum and the value at the center of the cage is around 70 meV, larger than kT at room temperature. This sodium displacement has been checked with a calculation using GGA, where the whole system was allowed to relax. In this case, we obtain a sodium separation of 5.2 Å.

The energy curves can be fitted around the potential well with a parabola [see Fig. 2(b)]

$$E = E_0 + \frac{1}{2}K(Q - Q_0)^2 \text{ and } \omega = \sqrt{\frac{K}{\mu}},$$

where K is the force constant, Q the normal coordinate of the vibrational mode, the 0 subscript referring to the equilibrium value; ω is the vibrational frequency and μ the reduced mass. For one Na in a cage, we have $\mu = m_{\text{Na}}$ and $Q - Q_0 = d$, d being the sodium displacement from the equilibrium position, and for two sodium atoms in adjacent Si_{28} cages, we have $\mu = m_{\text{Na}}/2$ and $Q - Q_0 = 2d$. In this case, we get a phonon energy of 8.7 meV, in good agreement with the experimental value of 6.6 meV for the vibrational mode assigned to the sodium in Si_{28} cages.¹⁹ For Na in $\text{Si}_{28}\text{H}_{28}$, we get a phonon energy of 2.7 meV far from the experimental value. Concerning the $\text{Si}_{20}\text{H}_{20}$ cage, the parabolic fit gives a phonon energy of 15.9 meV, very close to the experimental values obtained by neutron scattering¹⁹ or Raman spectroscopy.¹⁷ In addition, EXAFS oscillations weakly depend on the temperature between 20 and 300 K, which emphasizes that sodium atoms are trapped in a significant potential well.

IV. DISCUSSION

EXAFS experiments have provided evidence that the sodium atoms move away from the center of the Si_{28} cages. Whereas these experiments are not able to tell if the sodium displacements are correlated or not, *ab initio* calculations can account for this observation in term of a symmetrical displacement of sodium atoms in adjacent Si_{28} cages. This phenomenon is tantamount to a “dimer” formation. The resulting Na-Na distance is about 4.3 Å, to be compared with the 3.1 Å bond length of Na dimer in gas phase. The sodium lifts the initial T_d symmetry towards C_{3v} symmetry in the Si_{28} cage and $\bar{4}3m$ point symmetry lifts to $3m$. EXAFS, which is a local probe, cannot tell how the “dimers” are distributed in the crystal and in particular if there is a long-range order. For instance, each $\text{Na}@Si_{28}$ could be displaced in the same direction (111), equally distributed along the four equivalent directions [(111), (11 $\bar{1}$), (1 $\bar{1}$ 1), and ($\bar{1}$ 11)], or randomly distributed. Table I reports the crystallographic data for describing the dimerized clathrate, in the case of just one direction of dimerization. The symmetry operations for Na in the Si_{28} cages are not compatible with point symmetry in

cubic group but retains the F lattice. For simplicity, the true description of the lattice corresponds to the superposition of the $Fd\bar{3}m$ lattice for $\text{Na}_4\text{Si}_{34}$ (Si_{20} cages fully occupied) with a F cubic lattice without group symmetry having a basis of two Na atoms (Na in Si_{28} cages).

Such a displacement of Na atoms should have effects on the x-ray diffraction (XRD) patterns of $\text{Na}_2\text{Si}_{34}$ and $\text{Na}_6\text{Si}_{34}$. We have calculated the XRD pattern for the two stoichiometries with all the Na atoms in Si_{28} cages dimerized. As already discussed, we do not know how the dimers are distributed. We have therefore tried two configurations with a long-range order (superstructure): only (111) as dimerization direction, or an equal distribution along the four possible directions of dimerization. These two cases correspond to minor changes in the diffraction spectra (that would be diluted in the typical experimental noise). The most significant effect of dimerization in the XRD pattern is the change of the intensity of the (333), (531), and (660) peaks. In particular the ratio $I(333)/I(531)$ is modified with the sodium displacement and for both $\text{Na}_2\text{Si}_{34}$ and $\text{Na}_6\text{Si}_{34}$ samples dimerization can improve the agreement between calculated spectra and experimental ones. Using the data of Ramachandran *et al.*,³² we find that the calculated ratios $I(333)/I(531)$, with the sodium atoms at the center, are, respectively, 39 and 21 % larger than the experimental value for $\text{Na}_2\text{Si}_{34}$ and $\text{Na}_6\text{Si}_{34}$, whereas with dimerization (displacement of 0.65 Å), they are, respectively, 8% larger and 2% lower. It is important to note that this improvement is obtained without any parameter optimization.

NMR results must also be reconsidered in the light of Na displacement. The assignment of the peaks of ^{23}Na NMR spectra was first controversial^{8,10} but has been addressed recently by He *et al.*¹³ The authors discuss the assignment of the two peaks to the sodium in each type of cage, for $\text{Na}_6\text{Si}_{34}$ through their anisotropy. Making the assumption that the sodium atoms are at the center of the cages, the point symmetry is $\bar{4}3m$ in Si_{28} and $\bar{3}m$ in Si_{20} . With these symmetry arguments, the authors conclude that the anisotropic peak corresponds to $\text{Na}@Si_{20}$ and the isotropic one to $\text{Na}@Si_{28}$. Moreover, the ratio of the intensities seems to corroborate this assignment. However, even in the anisotropic Si_{20} cage, the quadrupolar coupling constant is very small, and Latturmer *et al.*¹² find that there is no quadrupolar effect for $\text{Na}@Si_{20}$ in their ^{23}Na NMR spectra of $\text{Rb}_8\text{Na}_{16}\text{Si}_{136}$. Since the sodium can move away from the center of the Si_{28} cages, the corresponding peak should be anisotropic, perhaps much more than the peak of Na at the center of the Si_{20} cages. The sodium displacement can be a dynamic phenomenon: the Na atoms may be able to “jump” between the four off-center equilibrium positions in the Si_{28} cages. The apparent disagreement between our results and the conclusions of He *et al.* could be due to the difference in the characteristic times of NMR and EXAFS processes. Such a motion has already been envisaged for fullerenes encapsulating a La atom.³³

As far as ESR is concerned, Roy *et al.*¹⁴ have shown that there are significant indirect interactions between Na atoms in adjacent Si cages. Yahiro *et al.*¹⁵ have observed a signal

assigned to Na_2^+ dimers in $\text{Na}_{0.75}\text{Si}_{34}$, but the nature and location of these dimers are not clear. At such a low dopant concentration, if the distribution of sodium was homogenous throughout the material, there should be less than one Na atom for every two Si_{28} cages. The observation of Na dimers proves first, that at this particular stoichiometry sodium is not homogeneously distributed, and second, that dimerization may actually occur in the clathrate.

Even though the Na displacement is unambiguous, its physical origin is not clear yet. On a pure energetical point of view, we can describe it as a Jahn-Teller effect.^{34,35} The displacement could induce a small gap at the Fermi energy and hence lower the total energy of the compound. Moreover, this hypothesis is consistent with ESR measurements¹⁵ showing that, contrary to calculation predictions, $\text{Na}_2\text{Si}_{34}$ is a semiconductor with a gap of approximately 0.01 eV. However, it does not tell us the underlying physical phenomenon (cage effect, local effect, collective effect?), whereas the interaction of two Na atoms in two adjacent Si_{28} cages seems to be of prime importance. As deduced from the potential energy curve (see Fig. 2), the coupling between Na and a Si_{28} cage is rather weak, particularly along the direction to an adjacent Si_{28} cage (axis of a hexagonal face). Correspondingly, it allows an electronic interaction between Na atoms in two neighboring Si_{28} cages. These atoms can then follow their trend to form a dimer [the dimerization energy in the gas phase is as high as 0.75 eV (Ref. 36)]. Although the Na states must be less hybridized with those of Si in Si_{28} than in Si_{20} cages, as it has been pointed out by Smelyansky *et al.*,³⁵ the sodium atoms interact in a complicated way with the silicon lattice and with Na neighbors. This shows, once more, that these host-guest compounds cannot be regarded as usual doped semiconductors.

Furthermore, the fact that Na dimers are still present in $\text{Na}_6\text{Si}_{34}$ shows that the Na atoms in Si_{28} cages are weakly affected by the presence of other atoms in Si_{20} cages. The dimer formation can be regarded as a local phenomenon restricted to two adjacent Si_{28} cages. Indeed, the simple system $\text{Na}@_{\text{Si}_{50}\text{H}_{44}}$ can account for the Na displacement. There is probably, in addition, a collective effect of the clathrate crystal. However, such an effect needs accurate calculations and is still a great challenge. This dimerization may be another path to get a better understanding of the electronic properties of clathrates.

A similar phonon instability, the position at the center of the cages being unstable, has already been obtained in the calculations of Dong *et al.*²⁹ for germanium clathrates doped with various elements. The so called “rattling” modes of

doping atoms are very important for the thermal properties of clathrates. Moreover, Tse *et al.*³⁷ have recently shown that, according to calculations, the same instability occur under high pressure in K_8Si_{46} and could be related with the high pressure phase transitions in type-I clathrates.^{6,37} Even more recently, Kume *et al.*³⁸ have observed high pressure transitions in $\text{Ba}_8\text{Si}_{46}$, using Raman spectroscopy, where the vibrational modes of Ba in the large Si_{24} cages disappear around 7 GPa and seem to reappear at higher pressure. This emphasizes how important the guest-host interactions are in these cage-like materials. The displacement of the doping atoms can indeed have a great impact on the clathrates properties.

V. CONCLUSION

We have provided clear evidence for the guest displacement in silicon clathrates and its physical origin has been discussed in terms of dimerization and not only of phonon instability. These instabilities are of great importance in type-I clathrates where they can be related to phase transitions. Moreover, the displacement of the sodium atoms in Si_{28} cages may significantly affect many physical properties of the type-II clathrates. Most of them must be, therefore, revisited at the light of Na dimerization. Furthermore, Na doped clathrate II are challenging materials for numerical simulations. The dimer formation still needs to be simulated for $\text{Na}_6\text{Si}_{34}$. In addition, the connection between Na dimerization and the appearance of an insulating gap at the Fermi level of $\text{Na}_2\text{Si}_{34}$ has not been obtained in calculations yet. Both issues would require calculations with a very accurate k -space sampling. It might also be worth investigating the role of electronic correlations between Na atoms in Si_{28} cages.³⁹ Eventually, one exciting issue would either be the synthesis of Si_{34} doped with other elements close to Na such as Li or K (or a mixture of these elements with Na), or the synthesis of $\text{Na}_2\text{Ge}_{34}$ (in which the Ge_{28} cages are larger and therefore should couple even more weakly with sodium) and check whether the dimer formation persists or not. This investigation could provide the value of the coupling between the guest atom and the host network required for the dimer formation.

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